Final Report

Principal Investigator: Xianfan Xu, Purdue University

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This project is to develop techniques for controlling conductive thermal transport through excitation and manipulation of coherent phonons in a material. Fundamental studies of coherent phonon generation and interactions with other energy carriers were carried out for the development of the technique. The main method employed in this project is a temporal pulse shaping technique to generate femtosecond laser pulse trains and to excite, enhance, and/or suppress coherent phonons in a material. The method developed was also used to investigate phonon scattering and energy transfer in many emerging materials of engineering importance. Major accomplishments of this project include:

(1) Developed method and experimental apparatus for generating ultrafast laser pulse trains and method and experimental apparatus of using ultrafast laser pulses to excite and manipulate coherent phonons in materials.
(2) Demonstrated that coherent phonons can be used to control thermal transport and phase change in a material.
(3) Utilized control phonon generation and manipulation to investigated phonon dynamics and thermal transport in a number of materials, in particular, nanoscale materials including superlattices, filled-skutterudites (a thermoelectric material), and quantum dots.

Details of these results are described below:

(1) Development of method and experimental apparatus for generating ultrafast laser pulse trains and method and experimental apparatus of using ultrafast laser pulses to excite and manipulate coherent phonons in materials.

We have developed an experimental apparatus for generating ultrafast pulse trains with 50 fs pulse durations, and use these pulse trains to manipulate phonon vibrations. In Figure 1, we produce a pulse train of four pulses, with different pulse-to-pulse separation times, and observe their effects on phonon vibration, i.e., stronger phonon vibration is obtained when the pulse-to-pulse separation time matches phonon vibration, and weaker phonon vibration is obtained when the pulse-to-pulse separation time is out of phase with phonon vibration. This is termed coherent control of phonon vibration. In addition, we have observed phonon softening (decrease in phonon vibration frequency) at high laser intensity.

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14. ABSTRACT
This project is to develop techniques for controlling conductive thermal transport through excitation and manipulation of coherent phonons in a material. Fundamental studies of coherent phonon generation and interactions with other energy carriers were carried out for the development of the technique. The main method employed in this project is a temporal pulse shaping technique to generate femtosecond laser pulse trains and to excite, enhance, and/or suppress coherent phonons in a material. The method developed was also used to investigate phonon scattering and energy transfer in many emerging materials of engineering importance.

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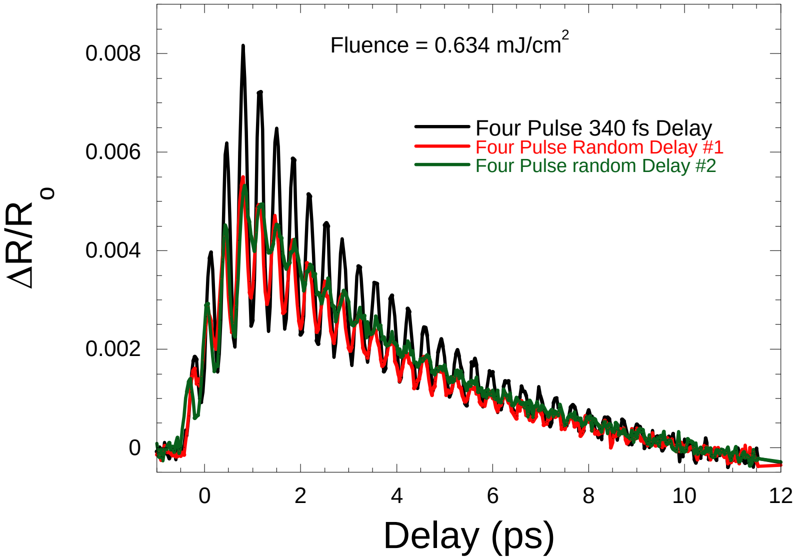

Fig. 1: Coherent oscillation in Bi, generated by four pulses. Black line: the four pulses are separated by a time interval corresponding to the vibration period of Bi phonon mode. Red and green lines: the four pulses are separated by a time interval different from the vibration period. Apparently, when the pulse-to-pulse separation is in synch with phonon vibration, the phonon vibration is enhanced; whereas when the pulse-to-pulse separation is out of phase with the phonon frequency, phonon vibration is suppressed (green line).

(2) Demonstration of coherent control of thermal transport and phase change.

One indication that phonon oscillation has a large effect on thermal transport is that material is damaged differently with different types of pulse trains. In Figure 2, the Bi surface is irradiated by two pulses, with different pulse-to-pulse separation time, but the same total energy. (Each experiment was done six times, shown vertically in the figure.) It can be seen that there are clear differences in the surface morphology, even the total laser energy is the same. A detailed analysis of the materials damage allowed us to determine the influence of phonon vibration on energy transfer.

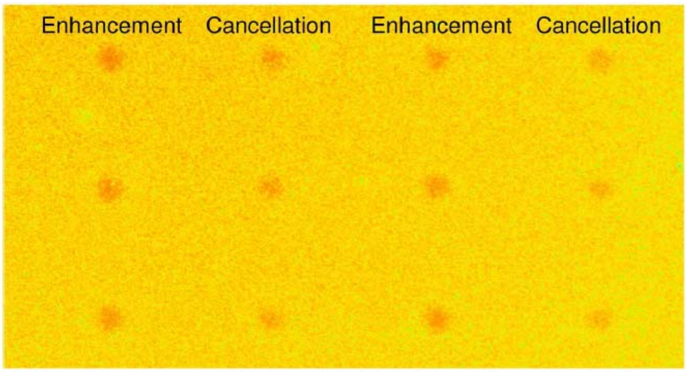

Fig. 2: Optical micrograph of surface of Bi irradiated by two laser pulses for phonon enhancement (column 1 and 3) and phonon cancellation (column 2 and 4). The total energy of the laser pulses are the same.

Figure 3 shows the multi-pulse damaged area as a function of laser fluence for 5,000 (a) double-pulse and (b) four-pulse excitation designed to enhance and cancel coherent phonon oscillations. It is seen that for both cases, the damage areas caused by enhancing phonon oscillations are larger than those when phonon oscillations are suppressed. It was also found for double-pulse excitation, the minimum total fluence required for damage with 5,000 pulses was 3.2 mJ/cm^2 for phonon enhancement and 3.9 mJ/cm^2 for phonon cancellation. For four-pulse excitation, a total laser fluence of 5.9 mJ/cm^2 was needed to damage for phonon enhancement and 6.3 mJ/cm^2 was needed for phonon cancellation. The differences in the damage area and in the minimum fluence required to obtain multi-pulse damage when the coherent phonon oscillations are enhanced and cancelled indicate the effect of the coherent phonons on thermal transport and materials phase change.

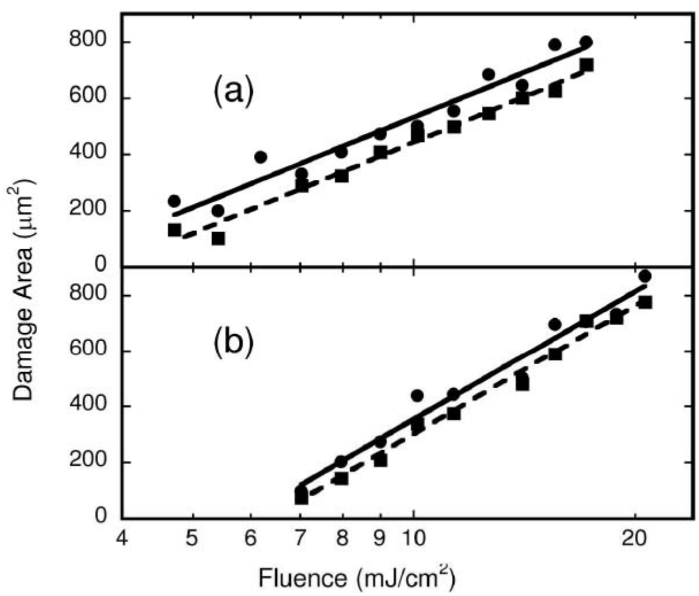

Fig. 3: Area of visible damage as a function of the incident pulse fluence for 5,000 (a) double-pulse and (b) four-pulse pulse trains designed to enhance and cancel coherent phonon oscillations.

(3) Investigations of phonon dynamics and thermal transport in materials

We used the method developed in this projecgt to investigate phonon dynamics in a number of materials, including Bi_2Te_3, Sb_2Te_3, and Bi_2Te_3/Sb_2Te_3 superlattice and misch-metal filled skutterudites. These studeis reveal phonon interactions with other energy carries, physical boundaries, and other modes of phonons, and help to gain a better understanding on the thermal transport process in these materials and methods to obtain the desired thermal transport properties.

Figure 4 shows optical phonon oscillations in Bi_2Te_3/Sb_2Te_3 superlattice at different laser fluences. By comparing the coherent phonon lifetimes, it was found that the phonon scattering rate (inverse of lifetime) in superlattice is significantly higher than those in Bi_2Te_3 and Sb_2Te_3. This represents the first direct measurement of coherent phonon lifetime reduction in superlattice structures, consistent with the observed reduction in thermal conductivity in superlattices. The interaction/scattering between phonon-electrons, phonon-phonon, and phonon/interface have all been determined.

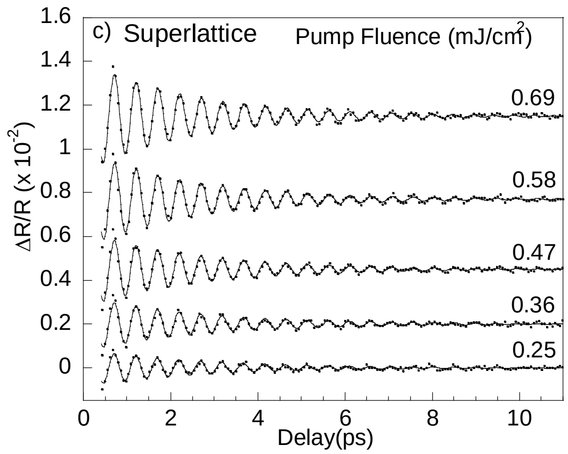

Fig.4 . Coherent phonon vibration signal for Bi_2Te_3 / Sb_2Te_3 superlattice.

We also developed methods for investigating acoustic phonon scattering in nano-engineered materials. Measurements of acoustic phonons are important as acoustic phonons are directly related to heat transport. Acoustic phonons were excited using a femtosecond pulse at the front of the sample surface, then measured when they were reflected back to the surface from the thin film – substrate interface using another femtosecond laser beam. The goal of these measurements is to understand the phonon scattering at interfaces, and therefore to understand the mechanisms of thermal conductivity reduction which is desirable for thermoelectric materials.

Our results indicate that there is significant phonon scattering in superlattices (Fig. 5b and 5c), where as scattering in bulk film sample is insignificant (Fig. 5a). Further analyses indicated a decrease of acoustic phonon velocity resulted from folding and flattening of phonons branches. Therefore, both the interface scattering and a lower phonon group velocity contribute to suppressing the heat transfer process. In addition, the deviations from acoustic mismatch theory have been observed.

We also invesitgated phonon dynamics in a number of other nano-engineered materials, including vibrational behaviors in misch-metal filled antimony skutterudites, an important thermoelectric materials which has great potential to be used for energy harvesting from waste heat. Figure 6 shows the detected vibration signatures of the filled elements. The reduction of lattice thermal conductivity – desirable for thermoelectric materials, over a wide temperature range can be explained using the measured resonant vibrational frequency which was obtained by performing Fourier transform on the data shown in Fig. 6. Our findings revealed that the reduction of lattice thermal conductivigty is a result of scattering of acoustic phonons due to the resonant interaction between guest atoms and lattice phonons.

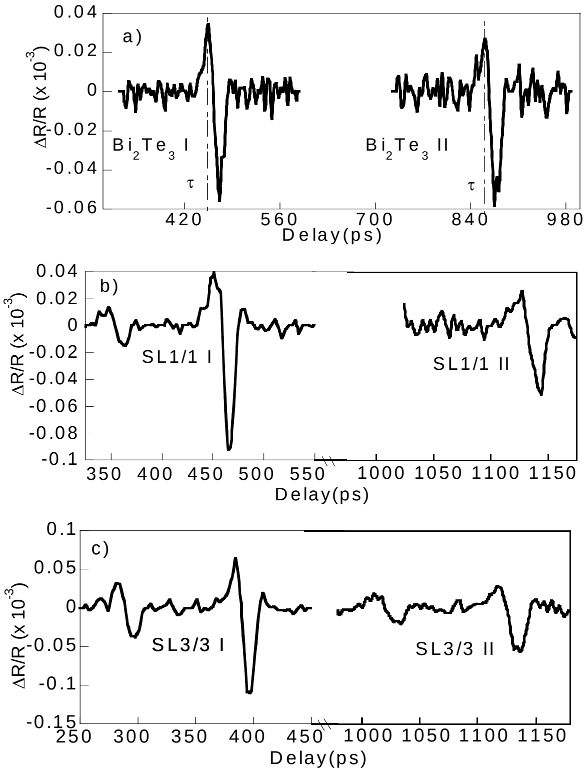

Fig. 5: Phonon amplitude measured in (a) bulk Bi_2Te_3 film with difference thicknesses, (b) 1 nm Bi_2Te_3 /1 nm Sb_2Te_3 superlattice with different thicknesses, (c) 3 nm Bi_2Te_3 /3 nm Sb_2Te_3 superlattice with different thicknesses. It is seen that phonon scatting in bulk films is insignificant (no visible change in phonon amplitude), whereas phonon scatting in the two superlattice samples is evident.

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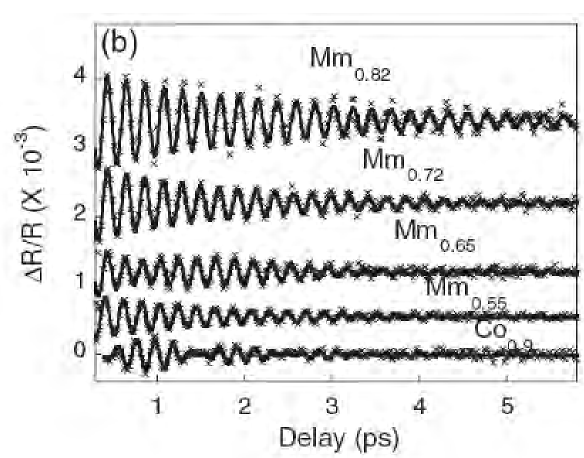

Fig. 6: Oscillation in filled-skutterudites. Relationship between these vibrations and thermal conductivity reduction was established.

Summary

In summary, this AFOSR sponsored project has resulted in significant accomplishments in the developoment of advanced laser-based technologies for generating and manipulating coherent phonons. The technique is used for the control of thermal transport and phase change. In addition, the method developed was used for investigating phonon dynamics and thermal transport in many materials, providing fundamental understandings of thermal transfer relevant to their engineering applications. It is expected that the knowledge and experimental tools developed in this work will continue to make contributions in thermal sicnece research in emerging materials.

List of Publications and Presesntatins:

Journals:

1. Wu, A.Q., Xu, X., and Venkatasubramanian, R., 2008, Ultrafast dynamics of photoexcited coherent phonon in Bi_2Te_3 thin films, Appl. Phys. Lett., Vo. 92, p. 011108. Also selected for publication in the February 2008 issue of Virtual Journal of Ultrafast Science.
2. Y. Wang, X. Xu, and R. Venkatasubramanian, 2008, "Reduction of Coherent Phonon Lifetime in Bi_2Te_3/Sb_2Te_3 Superlattices," Appl. Phys. Lett., Vol. 93, p. 113114. Also selected for publication in October 2008 issue of Virtual Journal of Ultrafast Science.
3. Wang, Y., Xu, X., and Yang, J., 2009, Resonant oscillation of misch-metal atoms in filled skutterudites, Phys. Rev. Lett., Vol. 102, p. 175508. Also published in June 2009 issue of Virtual Journal of Ultrafast Science.
4. Wang, Y., Liebig, C.M., Xu, X., Venkatasubramanian, R., Acoustic Phonon Scattering in Bi_2Te_3/Sb_2Te_3 Superlattice, Appl. Phys. Lett., Vol. 97, p. 083103. Also selected for the September 2010 issue of Virtual Journal of Ultrafast Science
5. Liebig, C.M., Wang, Y., and Xu, X., Controlling phase change through ultrafast excitation of coherent phonons," Opt. Exp., Vol. 18, pp. 20498-20504.
6. Liebig, C.M., Srisungsitthisunti, P., Weiner, A.M., Xu, X., Enhanced machining of steel using femtosecond pulse pairs, Appl. Phys. A., Vol. 101, pp. 487-490.

Conferences and Seminars:

1. Wang, Y., Xu, X., 2009, Investigation of Phonon Scattering and Thermal Conductivity Reduction in Thermoelectric Materials using Ultrafast Time-resolved Optical Measurements, Proceedings of the ASME 2009 Heat Transfer Summer Conference, Paper # HT2009-88210, San Francisco, CA, July, 2009.
2. Wu, A.Q., Xu, X., Weiner, A.M., 2008, Coherent Phonon Excitation and Manipulation in Bismuch using Temporally Shaped Ultrafast Pulses, Conference on Lasers and Opto-electronics, San Jose, CA, May 2008 (**invited**).
3. Xu, X., 2008, "Ultrafast and nanoscale diagnostics of energy transfer process" 6^{th} US-Japan Joint Seminar on Nanoscale Transport Phenomena – Science and Engineering, Boston, MA, July 2008. (**invited**)
4. Xu, X., 2008, Ultrafast diagnostics of energy transfer in photovoltaic materials," SPIE Optics & Photonics, San Diego, CA, August 2008 (**invited**).
5. Wang, Y., Xu, X., "Dynamics of photoexcited coherent phonon in Bi_2Te_3, Sb_2Te_3, and Bi_2Te_3/Sb_2Te_3 superlattices," at Ultrafast Phenomena in Semiconductors and Nanostructure Materials XIII, SPIE Photonics West, San Jose, CA, January 2009 (**invited**).
6. Xu, X., 2009, "Ultrafast Energy Transfer in Thermoelectric Materials," joint Indo-US workshop on Nanostructured Materials and Interfaces, Purdue University, March 2009.
7. Bao, H., Habenicht, B.F., Prezhdo, O.V., Ruan, X., Xu, X., "Temperature dependence of hot carrier relaxation in PbSe nanocrystals: an ab initio study" in Nanoscale Photonic and Cell Technologies for Photovoltaics II, edited by L. Tsakalakos, Proceedings of SPIE Vol. 7411 (SPIE, Bellingham, WA 2009) 741106. (**invited**)
8. Liebig, C., Wang, Y., and Xu, X., "Effect of Coherent Excitation on Surface Modification," Conference on Laser Ablation (COLA), Singapore, November 2009.
9. Xu, X., NSF/DOE Thermoelectrics Partnership: Thermoelectrics for Automotive Waste Heat Recovery, DOE Thermoelectrics Workshop, San Diego, CA, January 2011.
10. Xu, X., "Effect of temporal pulse shaping and coherent excitation on laser microfabrication" Spring MRS Meeting, San Francisco, CA, April 2011. (**invited**)

11. Wang, Y., Xu, X, and Venkatasubramanian, R., Phonon Scattering in Bi2Te3/Sb2Te3 Superlattice, Proceedings of the ASME/JSME 2011 8th Thermal Engineering Joint Conference, Paper No. aJTEC2011-44012, Honolulu, HW, March, 2011.

Other invited talks:

1. "Ultrafast Energy Transfer in Nanoscale Energy Conversion Materials," April 2008, Tsinghua University.
2. "Ultrafast and near field laser processing and diagnostics," June 2008, University of St. Etienne, France.
3. "Ultrafast excitation and detection of coherent phonons in energy conversion materials," Department of Physics, Purdue University, October 2008.
4. "Dynamics of Energy Transfer in Thermal Electric Materials," Department of Mechanical Engineering Distinguished Seminar Series, Iowa State University, March 2009.
5. "Ultrafast Energy Transfer in Energy Conversion Materials," Department of Mechanical Engineering, Rutgers University, October 2009.
6. "Fundamentals of Energy Transfer in Nanoscale Energy Conversion Materials," Kenninger Family Lecture in Renewable Energy and Power, School of Mechanical Engineering, Purdue University, November 2009.
7. "Fundamentals of Energy Transfer in Nanoscale Energy Conversion Materials," Department of Mechanical Engineering, University of Houston, November 2009.
8. "Ultrafast Energy Transfer in Nanoscale Energy Conversion Materials," the National Renewable Energy Laboratory, Golden, Co., February 2010.
9. "Energy Transfer in Nanoscale Energy Conversion Materials," University of Texas at Dallas, Dallas, TX, April 2010.
10. "Laser Optics and Laser Matter Interactions," at the NSF Work shop, Principles of and Recent Advances in Laser Micro/Nano Manufacturing Processes, Northwestern University, Evansville, IL, June 2010.
11. "Laser-induced Heat Transfer," at the NSF Work shop, Principles of and Recent Advances in Laser Micro/Nano Manufacturing Processes, Northwestern University, Evansville, IL, June 2010.
12. "Fundamentals of Laser-matter Interaction and Its Application in Laser Based-Manufacturing and Energy Transfer Analysis," Xi'an Jiao Tong University, Xi'an, ShanXi, China, June 2010.
13. "Energy Transfer in Nanoscale Energy Conversion Materials," Haerbin Institute of Technology, Haerbin, Liaoning, China, June 2010.
14. "Field Enhancement using High Gain Bowtie Nano-Antenna and Antenna Array and Its Engineering Applications," Near Field Optics-11, Beijing, China, September 2010.
15. "Energy transfer in nanoscale energy conversion materials," University of Texas - Austin, Austin, TX, September 2010.
16. "Energy transfer in nanoscale energy conversion materials," Georgia Institute of Technology, Atlanta, GA, September 2010.